

ExxonMobil employee being treated for HF exposure

## Hydrofluoric Acid Incidents in Torrance & Elsewhere<sup>1</sup>

### *A partial chronology*

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During the early 1990's the Mobil Oil Corp. campaigned to convince the city that modified hydrofluoric acid (MHF), although volatile and lethal at low levels of exposure, is safe enough to use in the middle of Torrance. They did this partly by claiming a significant accident can never ever possibly happen, estimating that a MHF leak could pose a level of "significant concern" to 33.7 people in the neighborhood once in 285,000 years.<sup>1,2</sup>

An examination of prior hydrofluoric acid (HF) incidents reveals that such a claim is not credible. The primary value of risk analyses for toxic chemicals is to convince the public to accept the unacceptable and provide legal protection for those who accept public risk in the name of private profit. The release record documented in this report is proof that an accidental release of MHF can occur, due to human error, poor maintenance, or mechanical failure, and that emergency measures can fail for the same reasons. Releases haven't yet caused death and injury in the community because of dumb luck, not skillful operations.

Regulators don't have good data on the amount of HF/MHF that is accidentally released each year. That data is self-reported by the refineries and there are inconsistencies across agencies and over time. It isn't clear what motivation the refineries have to report actual amounts. According to the Torrance refinery's EPA Toxics Release Inventory (TRI) report, accidental releases of MHF/HF occurred every year but one from 1988 to 2014 (table, below).<sup>3</sup> The release amount for the entire period totaled 6,700 lb., for an average of 258 lb. per year. But according to ExxonMobil's AQMD "Hot Spots" Health Risk Assessment, average annual HF emissions were 343 lb/yr for 2006-2007.<sup>4</sup> TRI entries for those years average only 140 lb/yr (Table entries in red), less than half the Hot Spots estimate. A 1995 Torrance Fire Department report to the City Council listed only 8 HF incidents from 1979 to 1995. In fact, there were at least 9 substantial releases from 1987 to 1995 alone, and it's likely there were multiple releases from 1979 to 1986.

YEAR	'88	'89	'90	'91	'92	'93	'94	'95	'96	'97	'98	'99		
LBS.	750	250	250	380	385	350	350	410	410	430	310	620		
=====														
YEAR	'00	'01	'02	'03	'04	'05	'06	'07	'08	'09	'11	'12	'13	'14
LBS.	130	16	81	3	890	170	130	150	27	25	3	3	2	2

The public is even less informed than government agencies. The two largest releases, 890 lb. in 2004 and 750 lb. in 1988, went completely unreported in the press, as did most other significant releases. Even when reported by the press, release amounts are significantly understated. The third largest release, 620 lb. in 1999, was reported as "trace amounts of modified hydrogen fluoride." A 1999 Mobil public education pamphlet reported two releases over a five-year period totaling 298 lb.<sup>5</sup> Actually, releases occurred every year that period, totaling 2,180 lb.

MHF advocates boast that there is no documented incident in which HF exited the refinery. One wonders if it's the documentation that is lacking, not the incident itself. During the 1999 release of 620 lb. MHF, Crenshaw Boulevard was shut down for more than two hours and nearby schools ordered to shelter in place.<sup>6</sup> Such actions are not taken for the release of "trace amounts," as the press described the release, as we know from ExxonMobil's response to the September 6, 2015 release of 10 drops MHF per minute for hours.<sup>7</sup>

Even including 2004, the worst year ever, release amounts averaged two-thirds less starting in 2000, the first year after the Exxon Mobil merger. This is likely due more to ExxonMobil secrecy and evasiveness than to improvements in safety. After all, Mobil had spent millions of dollars in safety improvements by 1995 and had been under unusual scrutiny and oversight for a decade under the Consent Decree. ExxonMobil was always far

<sup>1</sup> This report is available at this link: <http://bit.ly/1qnnnok>

more secretive than the Valero in Wilmington, which is more open with MHF data and “safety” limitations. As the Chemical Safety Board (CSB) confirmed at their 1/13/2016 hearing, the 2/18/2015 explosion was a near miss on a MHF tank containing 50,000 lb. But ExxonMobil claimed the community was never in danger, refuses to accept that a near-miss occurred, and will not provide the Chemical Safety Board with the MHF unit information it has requested.

#### Partial History of HF-Related Incidents at Torrance ExxonMobil (Previously Mobil) Refinery

**1987-11-24 KOH Treater Fire.** 165 lb. HF released, 10 injured, a spectacular fire burned for two days<sup>8</sup> (41-hr fire), and \$17M damages.<sup>9</sup> “The cause of the fire was due to an over-pressurized potassium hydroxide propane treatment system. The vessel exploded and propelled into a central pipe rack, shearing hydrocarbon and flare lines. Additional fires resulted, which severely damaged the unit.”<sup>10</sup> “Leakage of hydrofluoric acid into a tank where it reacted violently with a potassium caustic is the probable cause.”<sup>11</sup> The explosion in the Alkylation Unit “shot a fireball 1,500 feet into the air, blasted the windows out of nearby houses and generated allegations of broken eardrums, back pain and lung damage.”<sup>12</sup> The HF release was caused when an employee accidentally opened a valve to a pipe containing acid vapors, according to the Fire Department. The report said refinery workers were able to shut the valve within five minutes. Torrance authorities closed Crenshaw Boulevard for several hours on Nov. 25 and Nov. 29, 1987.<sup>13</sup> According to the 1995 Mobil Safety Advisor (SA) report, 165 lbs. of HF were released. Mobil knew that primary alarm systems and monitoring devices were not working. Instead of fixing them, they relied on periodic chemical tests and a backup alarm system. If they had only tested *the backup alarm system*, they would have realized *it was not even hooked up*. Mobil refers to this as “human error” instead of “cost-cutting.” According to the AQMD, there was a “lack of water to fight [the fire]... due to the improper work practices of contract labor hired by [Mobil].”<sup>14</sup> In 1988, the federal Occupational Safety and Health Administration conducted two investigations of Mobil. “The inquiry into the 1987 alkylation unit fire found four “serious violations” of federal safety regulations. OSHA defines a serious violation as one “where there is a substantial probability that death or serious physical harm could result and where the employer knew, or could have known, of the hazard.” Mobil paid a \$4,000 fine. The second OSHA investigation, which covered the entire plant, began in September, 1988. It led to 35 citations of Mobil, including 12 for serious violations.”<sup>15</sup> Mobil’s 2014 TCI report begins with 1988 and does not include 1987.

**1988.** Mobil’s 2014 TCI report states that 750 lb. of HF were released in 1988, the second largest reported release of HF from the refinery.<sup>16</sup> Yet no press report or other report on an HF release can be found.

**1989-06-27: A single drop**<sup>17</sup> of HF leaking from a flange or a **small leak of water containing HF**<sup>18</sup> splashes onto the face of a construction worker. The slow leak occurred in a relief gas scrubber that removes hydrofluoric acid. The leak had been going on for four days at the time of the accident. A 35-year-old man was hospitalized with a deep burn. Mobil said he was constructing the scaffolding so that workers could repair the leaking flange in the refinery’s alkylation unit. **Mobil’s TCI report says 250 lb.** of HF were released in 1989 but this was the only report found on a HF release.<sup>19</sup> But on March 8, 1989, a release of a volatile acid from the refinery sent “eight students and two teachers to the hospital with nausea, headaches, chest pains and dizziness.” Some but not all of the victims described a rotten egg smell, the odor of hydrogen sulfide, others as manure. The gas was most likely hydrogen sulfide, but the AQMD could detect no hydrogen sulfide at the school or refinery, so the question is still open. HF has a strong pungent odor, and victims’ had symptoms similar to HF’s: ‘If you took a breath of air, you wanted to throw up immediately,’ she said. ‘The teacher in the next room had chest pains. In my room, kids were gagging,’<sup>20</sup> “I started having pain in my throat. As it got worse, it went straight through my body, up my jaw and down my arms,’ she said. ‘I was getting more and more panicky. I couldn’t breathe, the pain was so severe.’<sup>21</sup>... [Another victim] felt as if her sinuses were on fire, that there was fire down her throat and burning in her chest.”

**1990-06-11 Alkylation Unit leaks “small amount” of HF.**<sup>22</sup> Mobil spokesman Jim Carbonetti at first disputed that any hydrofluoric acid had been released. He later conceded that a small amount leaked along with ammonia vapors being used to purge the alkylation unit. **Mobil’s TCI report says 250 lb.** of HF were released in 1990; this is the only report found.<sup>23</sup> A toxic cloud of choking vapors injured three workers at Mobil’s Torrance refinery on Monday night. All were contract workers from Serv-Tech Co. of Harbor City. It was their first day at the refinery. The impact of the vapors was almost instantaneous. “I saw a **big cloud, like a cloud you see in the sky**. I heard a roar noise,” said Delome. “I slid down the ladder like a monkey, and I ran about 30 yards.” He held his breath, he said, as long as he could, but he wasn’t out of danger. His first breath “cut the wind off to my

*lungs...I was just gasping. I started puking right away," he said.* Workers described the cloud as “**dense, white, ground-hugging vapors.**”<sup>24</sup> The workers complained of symptoms including shortness of breath, nausea, chest pains, eye and throat irritation, and burning sensations in the respiratory tract, and required hospitalization. Two were released after two days, and the third after three days in the hospital. The incident prompting an investigation by state and local officials under the heading of a release of acutely hazardous hydrofluoric acid. In the aftermath of the release, Torrance fire officials and the South Coast Air Quality Management District have moved to improve reporting of accidents at Mobil. Despite vocal public concern about safety there, top city officials did not learn of the accident until early Wednesday. Torrance Fire Chief Scott Adams, whose department learned of the release when its paramedics were summoned, did not find out about the accident until 30 hours after it happened, according to a memo written by Adams on Wednesday. Mobil did not notify the air quality agency about the release, but now has agreed to inform it any time a release of air-borne toxics causes injury, according to Arnold Stein, AQMD senior enforcement manager. Carbonetti said the apparent cause of the release was the failure of a half-inch fitting used during the purge of residual vapors from the alkylation unit.

**1991. 380 lb.** Mobil’s TCI report states that 380 lb. of HF were released in 1991,<sup>25</sup> but no press report on any HF release could be found.

**1992-07-15 Thermowell Breach.**<sup>26</sup> **32 lb. of HF** were reported released in a mechanical failure. Mobil’s TCI report states that 385 lb. of HF were released in 1992; this is the only report found.<sup>27</sup> No acid wafted off-site, Mobil and city officials claimed.<sup>28</sup> Battalion Chief Kenneth Hall, the Fire Department’s hazardous materials chief, delivered an inappropriately upbeat message for an emergency responder, “There is not one documented incident in which HF has extended beyond the fence line.”<sup>29</sup> After MHF’s operational failure in 1997 and the resulting slashing of additive concentration, in 1998 Hall joined with Safety Advisor Steve Maher, retired TFD Chief R. Scott Adams, and Mobil Public Affairs Manager Carolin A. Keith to write a book on how to communicate industrial risk to the public and government.<sup>30</sup> The book aimed to improve community “understanding” of risk, “precipitating improved acceptance” and “decreas[ing] potential for legal action by the community to enforce what it considers to be an equitable risk balance (this has occurred).” This statement is footnoted with a reference to the Mobil-Torrance Consent Decree. After retirement in 2003, Hall followed retired Torrance Fire Chief R. Scott Adams’ example by working as a consultant for Steve Maher’s firm, Risk Management Professionals (RMP). He was listed as a “key personnel” for RMP at least up to 2011.<sup>31</sup>

**1993. 350 lb.** Mobil’s TCI report states that 350 lb. of HF were released in 1993,<sup>32</sup> but no press report on an HF release could be found.

**1994-10-19 Coalescer Inlet Piping Hydrocarbon Release and Fire.** Reported as a **NEAR MISS**. The explosion occurred *50 feet from the refinery unit that uses hydrofluoric acid.*<sup>33</sup> Mobil’s TCI report states that 350 lb. of HF were released in 1994,<sup>34</sup> but this is the only press report that could be found. The Mobil Safety Advisor included this incident in his 1995 report, so the HF release probably occurred at this time.<sup>35</sup> *Cal/OSHA reassigned its primary criminal investigator in January 1995 after he was quoted in a local newspaper story expressing concern about the potential for an HF release in the explosion.* Mobil had complained to the agency. Cal/OSHA reassigns investigators to avoid jeopardizing an investigation if employers question their conduct, a Cal/OSHA spokesman said.<sup>36</sup> The explosion and fire injured 28 workers, at least 6 seriously,<sup>37</sup> and were the most serious at Mobil in seven years. It apparently occurred when flammable gases spewed from a pipeline that had been left disconnected.<sup>38</sup> After a five-month probe, Cal/OSHA investigators concluded that Mobil “willfully” failed to properly inspect refinery equipment during a series of events before the Oct. 19 explosion.<sup>39</sup> A butane gas explosion occurred after flammable gases were allowed to flow into a pipeline left disconnected after construction work.<sup>40</sup> Workers told the Daily Breeze safety procedures were not followed.

**1995. 410 lb.** Mobil’s TCI report states that 410 lb. of HF were released in 1995,<sup>41</sup> but no press report on a HF release could be found.

**1996-03** Two employees received chemical burns from *exposure to hydrogen fluoride*, state industrial accident reports show.<sup>42</sup> One was hospitalized.

**1996-09-07 [or 06].** A fire erupted that shook nearby residents out of their beds at 5:18 a.m., causing many of them to flee when they saw flames coming from one of the many towers. The fire appears to have been caused

by a gasoline leak at a pump in the platinum reformer unit. The fire occurred one block away from a toxic *hydrofluoric acid unit*, but a spokesman claimed there was no danger that that unit would explode.<sup>43</sup>

**1998-06 Release of ~10 lb. MHF.**<sup>44</sup> During truck delivery Crenshaw Blvd. closed. This may have been the first release of MHF since the refinery began using it — instead of HF — in 1997.

**1999-04-02: The total amount from MHF/HF releases for 1999 was 620 lb.,** the third highest yearly amount released since (at least) 1987.<sup>45</sup> But the only press report found for a 1999 release states that “trace amounts of modified hydrogen fluoride” were released on this date.<sup>46</sup> A

**Release of 288 – 300 lb. HF, not MHF.**<sup>47</sup> Three workers required hospital treatment after a broken pipeline spilled isobutane and *288-300 lb. of hydrofluoric acid* from the alkylation unit, **shutting down Crenshaw Boulevard** for more than two hours. Nearby schools were ordered to **shelter in place**. One of the injured workers, Don McDaniels, told TRAA that the release was actually 1,200 lb. HF and that Mobil/ExxonMobil has over the years shut off the additive pump *completely*.

**2001-07: AMOUNT UNKNOWN.** Nearby residents are told to **shelter in place** after a *leak of modified hydrofluoric acid* from the plant’s alkylation unit lasts at least 40 minutes.<sup>48</sup>

**2004. 890 lb.** According to the EPA Toxics Release Inventory, the largest amount of MHF and/or HF released in a single year since 1988 was 890 lb. in 2004.<sup>49</sup> No press or local government reports could be found regarding any HF or MHF release at the refinery in 2004. The National Response Center (NRC) Database of spills and accidents of oil and hazardous substances<sup>50</sup> lists three HF/MHF release incidents at ExxonMobil’s Torrance refinery. No information was provided on release amounts or duration of the releases. However, not all incidents are reported to the NRC and, generally, no independent verification or updates are performed on the ones that are reported.<sup>51</sup> It is unknown how much of the 890 lb. was released during each reported incident or if there were unreported incidents. All these releases were releases to the atmosphere, that is, airborne acid.

**2004-03-27 Release of HF (probably MHF but this is not specified) while off-loading “acid truck”**<sup>52</sup> **[Incident ID #67: 717169]** Amount and cause unspecified. Water was sprayed on the airborne acid, the Torrance Fire Department was called to the scene, and the AQMD was notified. The report notes, “Media Interest: none.”

**2004-11-11 Clamp on a pipe leaked MHF [Incident ID #161: 741101]**<sup>53</sup> At 10am. The only remedial action taken was to “isolate the line.” The report notes, “Media Interest: none.” MHF was specifically identified.

**2004-11-15 Process Piping Release. Close to 890 lb.? [Incident ID #163: 741451].**<sup>54</sup> 11:58 am, 74°F; 10 mph W wind. Hydrogen fluoride (either HF or MHF) was released from process piping due to unknown causes. According to one elusive source, “The pollution control scrubber faulted and released hydrogen fluoride for two days.”<sup>55</sup> Unknown amount, no estimated duration or release rate reported. The “remedial action” taken was to remove the piece of equipment from service. State and Local Agencies notified were the AQMD, the California Governor’s Office of Emergency Services (Cal OES), and the Torrance Fire Department. The State Agency Report Number for the incident was 90461. A toxic air release from a stationary source must be reported to Cal OES only if it “poses a significant hazard” to human health and safety, property, or the environment<sup>56</sup> (legal authority derived from California Health Code, HSC 25510).<sup>57</sup> Unless there was another significant unreported accident in 2004, this incident is likely to have been when most of the 890 lb. were released in 2004.

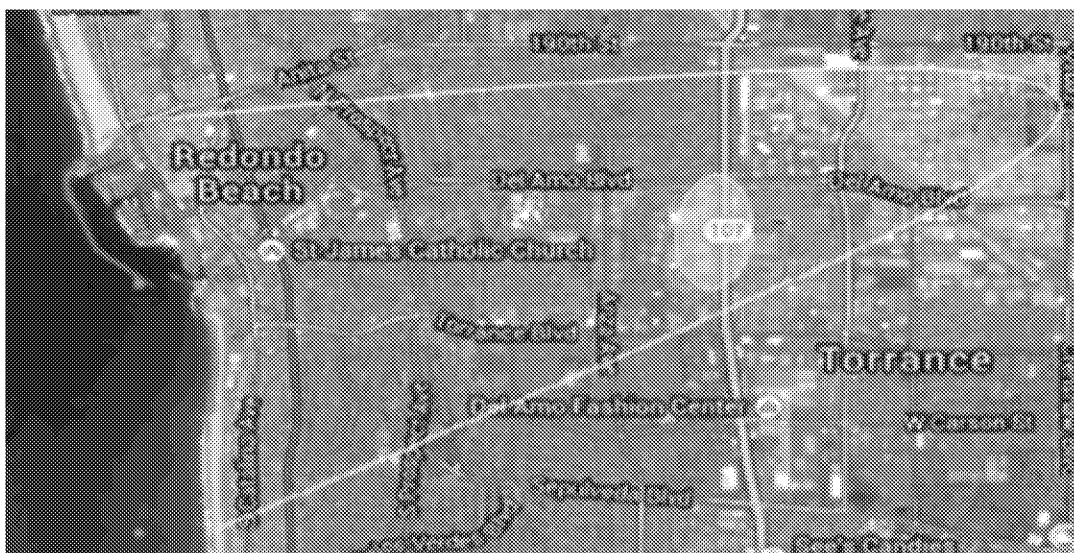
**2005-07-06 Relevant Lawsuit** filed by three employees of Mobil and its subcontractors but claiming to represent the interests of more than 500 employees of the company and subcontractors, says Mobil has *handled toxic materials improperly, failed to notify authorities about leaks and spills and put workers at risk*. Filed in U.S. District Court, it sought nearly \$2 billion in damages.<sup>58</sup> The outcome of the lawsuit is unknown, but it probably was triggered by events surrounding the 2004 release of 890 lb. MHF/HF.

**2015-02-18 NEAR MISS.** ExxonMobil’s 155,000 b/d Torrance refinery was hit by an explosion in an electrostatic precipitator (ESP), causing a fire which downed the fluid catalytic cracker, alkylation unit, reformer and hydrocracker. TRAA learned from a knowledgeable source in May 2015 this event was a *near miss for HF* given the location of the Alkylation unit, which the FCC feeds into. The alkylation unit is 100 feet

away from the ESP unit.<sup>59</sup> CBS News contacted TRAA members over the summer, and we provided them with information on MHF and the refinery (family members of one member are featured in the episode). In September 30, 2015, the story was aired on CBS Evening News, revealing that an 80,000 lb. piece blasted loose in the explosion landed just feet from the MHF tank (their photo, below).<sup>60</sup> If it had struck the tank *MHF would have been released*. A substantial hole could have resulted, with a high leakage rate of acid. Emergency water systems to suppress airborne HF could have been damaged by the impact, and would have been less effective against a large release, damaged or not.



The main debris plume from the February 18 explosion reveals the direction that the ground-hugging toxic cloud of HF created by the release would have drifted (below). Over 27,200 people live in this region, approximately 13,300 of them within 2 mi. of the alky unit. All would have been at risk of exposure to HF concentrations high enough to cause death or serious & irreversible injury to most with short exposure. Areas adjacent to this region would also have had a risk of exposure to HF at lower concentrations. Even they would have required prompt medical attention to prevent possible negative health effects from fluoride exposure.



CBS interviewed Vanessa Sutherland, the Chemical Safety Board Chair. She stated that only dumb luck had averted a catastrophe. "We were really, really lucky." The explosion was a "near miss" on the MHF tank. "It could have been much more catastrophic... If I were in the community I absolutely would be concerned." ExxonMobil announced that the community was never in any danger.

The ESP exploded as contract workers were doing maintenance on the nearby fluid catalytic cracking unit, or FCC. "Contractors working on the FCC to fix the expanders," a source said, adding that an injection of ammonia on top of the flue gas stream caused a pressure buildup, which resulted in the ESP unit explosion.<sup>61</sup> The

"refinery unit that was damaged by an explosion was already offline for unplanned maintenance when the fire occurred... The unit had been offline for two days because of problems when a different piece of equipment exploded, said the Oil Price Information Service, which tracks the oil industry. ...The area of the refinery had been offline because **the refinery was having problems with a recently repaired component called the alkylation unit**, according to a report by the Oil Price Information Service.<sup>62</sup> It wasn't clear if the recent repairs to the alkylation unit had anything to do with the explosion. ... The ... refinery has been fined more than \$100,000 over the past five years for health and safety violations, most of them minor, according to state records. The largest fine — \$18,000 — was for an accident that caused a 760-pound guide plate to land on a worker's foot. The refinery was last inspected in November [2014]."<sup>63</sup> PBF executive chairman Tom O'Malley also revealed on October 29, 2015 that ExxonMobil Torrance had "problems over the last two years at the refinery, including trouble with an alkylation unit and with the FCC."<sup>64</sup>

**2015-09-06 MHF release at ExxonMobil Torrance,**<sup>65</sup> 10 drops per minute for 15 hours. 2:35 a.m. discovery. "ExxonMobil mitigated the leak caused by the faulty clamp within 48 hours of the release. The company also removed tank 5C-31 from service, where the faulty nozzle was attached, to make repairs." ExxonMobil failed to follow established procedures to notify the Torrance Fire Department ExxonMobil site safety advisor sent an email notification to the Torrance Fire Department approximately 30 minutes later, and called the on-duty platoon commander at 8:38 am. Firefighters depressurized the vessel where the nozzle was leaking and sprayed it with water as a precaution. The TFD sent a "notice to improve" to the company, requesting that ExxonMobil come up with an "action plan" within two weeks to "improve the reporting of incidents at the refinery" and "ensure the safety of the community." City Manager LeRoy Jackson told the Breeze that the leak was "handled and resolved very quickly" and that "in those situations there are safety steps in place." Cal/OSHA investigated the release, finding on March 4, 2016 that "the leak was related to a temporary clamp that was installed on a three-inch nozzle flange following an earlier leak in 2011. The nozzle was not replaced until January, 2016. 'This is a case, a minor repair could have prevented workers at this refinery from exposure to a life-threatening acid,' said Cal/OSHA Chief Juliann Sum. 'These citations and penalties are a wake-up call that refineries must follow strict safety protocols to protect their employees.'" The citations issued included one willful-serious, "indicating the employer was aware of the hazardous condition and did not take reasonable steps to address it, and two general citations for ExxonMobil's failure to conduct a hazard analysis and identify and address the 2011 leak. Proposed penalties total \$72,120. ...Before ExxonMobil was allowed to restart operations in January, a complete inspection of the alkylation unit was conducted to ensure there were no additional leaking flanges or nozzles."

### Partial history of HF acid incidents at other refineries/plants

**1976-12-22 Ampol Refinery, Brisbane, Australia**<sup>66</sup> 28 tons, or about 7,000 gallons, HF released when a heavy steel bar fell onto a heat exchanger during a construction project. The heat exchanger was connected to the HF acid tank. *The entire acid inventory was released within 2 1/2 hours, for an average rate of about 50 gallons a minute.* Refinery workers controlled the release with fire sprays and fog nozzles and some of the gas was vented to a relief system where it could be neutralized. According to Ampol Refinery general manager Barry Woods, no one required medical treatment or first-aid.

**1977-07-08 Ampol Refinery, Brisbane, Australia.**<sup>67</sup> 7,000 gal. HF released, caused by the failure of a weld. According to Ampol Refinery general manager Barry Woods, one worker required medical treatment for inhalation, with no medical consequences.

**1980 Chemical Plant in Matamoros, Mexico.**<sup>68,69</sup> Approximately 10,000 gallons released. Believed to be the *largest release of HF on record*, the chemical poured out for 20 minutes from a ruptured valve at a rate of 500 gallons a minute [10,000 gallons], creating a dense cloud of toxic fumes. The Matamoros accident occurred at the Quimica Fluor plant, which manufactures hydrofluoric acid. The two employees who died were trapped in a building engulfed by fumes. An employee eventually donned a protective suit and shut off a valve to stop the release. A small community near the plant, which is in a rural area 4 1/2 miles outside Matamoros, was spared because *the wind was blowing the other direction*. Metallurgical analysis subsequently determined that the studs holding the valve cover had been weakened by HF.

**1986-01-04 Kerr-McGee Sequoyah Fuels nuclear-fuel processing plant, Gore, Oklahoma.**<sup>70,71</sup> 29,500 lb. of uranium hexafluoride was released, resulting in a plume of airborne HF. [On contact with moisture in the air,

uranium hexafluoride breaks down into uranyl fluoride, a slightly radioactive uranium compound similar to the natural ore, and HF.] One employee died as a result of inhaling hydrofluoric acid vapors, and 110 people were hospitalized. "It's a real madhouse down here with all these folks coming in," a Sequoyah Memorial Hospital spokeswoman said. Plant worker James Harrison, 25, of Vian, Okla., died of HF exposure at Sparks Regional Medical Center in Fort Smith, Ark., about four hours after the accident. He suffered from "toxic chemical exposure with hydrofluoric acid burns to the face and lungs." The incident occurred when an overloaded storage cylinder ruptured. One official said radiation exposure was not the most significant problem ...[HF was]. *Indications were that the cloud of hydrofluoric acid spewed and drifted as far as 18 miles.* Authorities said the cloud dissipated in winds of more than 20 m.p.h. [25 mph] about two hours after the first report of the leak. Interstate 40 was closed for two hours. A plant spokeswoman said it is located in a *sparsely populated area* with fewer than 10 homes within two miles of the direction the cloud drifted. All employees and residents living in the path of the cloud had to be examined by doctors as a precaution. A lawsuit filed on behalf of more than 50 Haskell County families sought \$110 million in damages from Kerr-McGee Corp., alleging their clients were injured by the plume. The Nuclear Regulatory Commission cited the facility for 15 health and safety infractions between 1978 and 1986.

**1987-10-30: Marathon Petroleum Co. Texas City, TX** 65,200 lb. released, 5800 people on 85 city blocks evacuated,<sup>72</sup> 1,037 people treated at hospital for respiratory (nose, lungs) problems and skin and eye irritations.<sup>73</sup> This is the largest known release of hydrofluoric acid in the US. "There were houses right up against the fence," said HF expert Dr. Ronald Koopman of Lawrence Livermore. *"The only thing that saved people was that the [HF] plume shot 200 feet up in the air, and it went about 900 meters downwind before it actually came down into the neighborhood. If it had squirted out sideways, it would have killed hundreds, if not thousands."*<sup>74</sup> This accident is proof that punctures above the liquid line of settled HF can be very significant in the amount released and size of HF cloud formed. "The Marathon oil incident is an example of a vapor release and could have had worse consequences had the leak occurred below the liquid level in the storage tank."<sup>75</sup> Firefighters attempted to saturate the cloud with water sprays, but the toxic cloud that was formed forced [evacuations and hospitalizations]."<sup>76</sup> The accident "resulted in a large hydrogen fluoride cloud blanketing a small area of the town,"<sup>77</sup> that was "reported to be two to three miles long and 0.5 to 1 mile wide."<sup>78</sup> The gas "defoliated trees in its path."<sup>79</sup> An epidemiologic study concluded, "the hydrofluoric acid exposure indeed caused health problems in the community that continued for at least 2 years after the accident."<sup>80</sup> The HF was released over a period of hours after a crane dropped a piece of equipment onto a pipeline containing HF. Marathon was performing a construction or repair project near the HF tank without draining it of its contents as should have been done. Damage occurred [the top piping was severed]<sup>81</sup> and the HF acid was released.<sup>82</sup> Based on this release, the South Coast Air Quality Management District developed a release scenario for a computer model of 70 gallons a minute for 100 minutes.<sup>83</sup> Attempts were made by citizens and Dr. Ralph Morris, Executive Director of the Galveston County Health District<sup>84</sup> to get Marathon to fund a long-term health study. Local health officials said that, in the absence of published scientific studies of exposure to similar leaks, a study of local residents was needed, especially concerning effects on children. Apparently, no study was funded.

**1988-03-19 Sun Co. Refinery, Tulsa, Oklahoma.**<sup>85</sup> 210 lb. HF released. "On March 19, 1988, at the Sun Co. refinery in Tulsa, Oklahoma, an accidental release of 210 pounds of hydrofluoric acid sent a cloud of hydrofluoric acid drifting five miles through downtown. *Had the accident occurred on a weekday, more people would have been injured.* One resident, living in the downtown area, said, "I didn't realize it was hazardous until I could see it leave orange particles everywhere...And then my eyes burned, my throat burned and my head ached."

**1989-06-27 Great Lakes Chemical.**<sup>86</sup> 1,320 lbs. HF released. Several bolts on an HF storage tank failed due to corrosion, and tank pressure forced the two halves of the isolator apart, releasing 1,320 pounds of HF. This incident is illustrative of an equipment failure situation in which HF can be released.

**1990-01-13 Powerine Oil Co., Santa Fe Springs, CA.**<sup>87</sup> Small HF release. Six employees were treated at a hospital for HF burns and possible vapor inhalation and released. Two other employees received respiratory treatment and were kept for observation in the hospital, one for 24 hours and the other for 48 hours.<sup>88</sup> The incident occurred when a *corroded pipe holding the acid ruptured*, creating a vapor cloud that employees diluted with water and stopped from drifting outside the refinery, according to oil company officials.

**1991 Southwestern Refining Co. in Texas.**<sup>89</sup> An accidental hydrofluoric acid release killed two workers and injured five others.

**1994-10-28 Illustrating the lethality of HF.**<sup>90</sup> A laboratory technician seated in a fume cupboard knocked over a small quantity (100-230 ml) of hydrofluoric acid onto his lap, splashing both thighs. The technician sustained burns to 9% of his body surface area, despite washing his legs with water at 6 lb./min. He was admitted to an intensive care unit for treatment. His right leg was amputated 7 days later. He **died** from multi-organ failure 15 days later.

**1995-1997 Sunoco Refinery, Philadelphia X 4.**<sup>91</sup> Between 1995 and 1997 this refinery had *four separate one-pound releases of hydrofluoric acid* at the injured one worker in each accident.

**1996-05-25 CITGO Refinery, Corpus Christi, TX.**<sup>92</sup> Smaller release.

**1996-09-20 CITGO Refinery, Corpus Christi, TX.**<sup>93</sup> Smaller release.

**1997-05-12 CITGO Refinery, Corpus Christi, TX.**<sup>94</sup> Uncontrolled release of unknown amount of HF. CITGO claimed that the fire at the alkylation unit "burned up" the HF [SH: HF is noncombustible, but thermal convection due to fire can disperse HF and make the cloud less dense] but there were thousands of reports of human exposure, vegetation damage, and corrosion in the Refinery Row neighborhoods in closest proximity to the site of CITGO's accident.

**2001-10-02 Valero Refinery, Paulsboro, New Jersey.**<sup>95</sup> 150 lbs. HF released. Because the wind was blowing toward neighboring Greenwich Township, a nearby elementary school was forced to secure all the children and staff in the gym by sealing the doors and windows with *duct tape and plastic*.

**2003-03-02 Marathon Ashland oil Refinery, St. Paul Park, Minnesota.**<sup>96</sup> Trace amounts HF released. 13 electricians working were hospitalized after being exposed. They had been hired to repair damage to the facility caused by a fire a few days earlier. While working, a pump leaked one cup of hydrocarbons with trace amounts of hydrofluoric acid, which immediately vaporized and entered their lungs.

**2005-01-21. Placid Refining, Port Allen, LA.**<sup>97</sup> 40 lbs of HF released. Incident was caused by a failure of a site glass on a process vessel. HF spewed out. Workers were injured.

**2005-07-09 ExxonMobil, Chalmette Refining (1376), Chalmette, LA.**<sup>98</sup> [Date was possibly the 10<sup>th</sup>]. 7.7 lb. HF released. Vessel was overpressured and went to flare.

**2007-01-02 Bayer Alumina Plant, Point Comfort, Texas.**<sup>99</sup> A thimbleful of HF released, 1 death. HF killed 37-year-old Alcoa technician John L Dorton in fewer than seven hours from the moment he inhaled the mist at the plant. He had opened a valve in the piping system of a vacuum monitoring line. He received immediate medical attention with calcium gluconate gel, a neutralizing agent, and was quickly taken first to one hospital and then another via life flight helicopter, for advanced medical treatment.<sup>100</sup> The root cause was determined to be the inadequacy of management standards, controls, and policies. They failed to require that technicians assigned to remove blockage within monitoring line stems use the appropriate special protective equipment. The company was cited and operations terminated until corrective actions were taken. The citation was terminated on February 2, 2007, one month later. Apparently no criminal charges were made; there's no record of a fine.

**2009-03-11 Sunoco Refinery, Philadelphia, PA:**<sup>101</sup> 22.3 lb. HF released, 13 contract workers treated at hospital. Ironworker James Jamison was welding and became engulfed in a "rain cloud" of noxious gas. "The smell was so intense," said Jamison, "I could feel it through my eyes, my nose, it was like a heat wave came over me." Jamison says he has permanent heart and lung damage as a result. *Sunoco is renovating the unit to use MHF.* The improvements also include new equipment to drain the alkylation unit in seven minutes if it springs a leak, averting disaster. But the improvements don't impress Savage, the head of the local Steelworkers union, who is a Sunoco employee. **"I don't want a less deadly form of HF," he said. "It really just needs to go away."** OSHA attributed the leak to *maintenance deficiencies* when it cited Sunoco for four violations and proposed a \$20,000 fine. The director of OSHA's Philadelphia Office said the Sunoco HF unit has a "history of leaks," which he partly attributed to a design change implemented in 1991, when engineers downgraded the

tubing that carries the acid through a heat exchanger. The design change involved replacing expensive Monel nickel-alloy tubes with cheaper carbon-steel tubes. OSHA said the tubes have a service life ranging from one month to 15 months between failures. "After conducting four inspections at the refinery from February 2009 to July 2010, OSHA cited Sunoco for 17 alleged violations, 11 of which had to do with process safety management. Sixteen of the 17 violations were classified as serious, one as a repeat infraction. OSHA found, for example, that the piece of equipment responsible for the HF release in Unit 433 had "an established history of tube leaks dating back to 1973."<sup>102</sup>

**2009-03-21 Transportation accident, Wind Gap, Pennsylvania.**<sup>103</sup> 5000 Residents from 944 households and animals including horses were evacuated for 15 hours. A tanker truck carrying more than 16 tons of hydrofluoric acid overturned 60 miles north of Philadelphia. The driver was treated for injuries and released; no other immediate reports of injuries. Emergency crews reported liquid dripping from the tanker's valves or piping, forcing them to don full-protection suits to stop the drip. The company responsible for a spill paid nearly \$139,000 to cover the costs of the incident.<sup>104</sup>

**2009-05-13 Honeywell, Baton Rouge, LA.**<sup>105</sup> 4 lbs. HF released. An internal chemical reaction occurred due to a nitrogen purge being cut off to the tank, leading to the release of HCL, HF, and Oxalic Acid.

**2009-07-19 CITGO Refinery, Corpus Christi, TX**<sup>106</sup> (photo, R). 42,000 lb. HF released, more than 4000 lb. of which exited the refinery despite a functioning HF water suppression system. "CITGO reported to the Texas Commission on Environmental Quality that approximately 21 (short) tons of HF released from alkylation unit piping and equipment."<sup>107</sup> *Prevailing winds carried it "toward the Corpus Christi ship channel and Nueces Bay away from population areas.* The CITGO refinery nearly exhausted their stored water supply for their water mitigation system during the first day, and after 11.5 hours following the incident CITGO began pumping salt water from the ship channel into their fire-water supply." Workers jury-rigged piping to use the nearby ocean water. The original cause of the "incident" was the unthreading of a single internal plug from a valve stem. This led to valve closure, violent shaking in the piping, and the breakage of connections. Hydrocarbons were released and ignited, leading to explosions and a fire that released HF and burned for several days. The fire critically injured one employee and another was treated for possible hydrogen fluoride exposure. One witness described the 10-inch steel pipe as moving like a cooked spaghetti noodle.<sup>108</sup>



**2009-07-14 Chalmette Refining (1376), Chalmette, LA.**<sup>109</sup> 3,257 lb. HF released. While an operator was flushing the HF Alkylation Unit's heat exchanger, a leak was discovered on the heat exchanger. The heat exchanger released chemicals into the cooling water system, which were subsequently released to the Mississippi River.

**2009-08-06 ExxonMobil Refinery, Joliet, Illinois.**<sup>110</sup> Trace amounts HF released. There was a sudden release of propane and "trace amounts" of hydrogen fluoride (HF) from the vicinity of a pump in the refinery's alkylation unit, which uses HF as a catalyst.<sup>111</sup> The leak did not ignite. One operator was transported to the hospital in critical condition suffering from serious HF chemical burns and remained there as of August 13, but was expected to live. A second operator was examined at the hospital and released. The unit's water deluge system was activated and the alkylation unit was shut down. Refinery personnel were instructed to shelter in place. The plant is one of ExxonMobil's six refineries that uses the HF process to make high-octane fuels, four of which are in the US, one in Canada and one in Europe.<sup>112</sup> The US Chemical Safety Board announced immediately that they would investigate. But in April 2010, CSB Chairman Bresland said that a new large-scale deployment to Washington State to investigate a Fatal Tesoro Refinery Accident will further complicate efforts to complete other important cases, including the CITGO refinery hydrogen fluoride release and fire in Corpus Christi, Texas and the Exxon Mobil refinery hydrogen fluoride release in Joliet, Illinois. I have been unable to locate the CSB report for this case; it was probably never completed.

**2010-03-23 Transportation, Tanker Truck, London, Ontario, Canada.**<sup>113</sup> The eastbound lanes and one westbound lane of 401, Canada's busiest freeway, were closed when a tractor-trailer hauling HF caught fire and its driver was injured. The driver discovered the rear of the trailer on fire, causing a tire to burst. Reportedly no acid leaked.<sup>114</sup>

**2010-06-09 Transportation, Honeywell Tanker Truck, London, Ontario, Canada.**<sup>115</sup> I-10 was closed after the tire of a Honeywell tanker truck carrying hydrofluoric acid caught on fire. The back end of the truck burned but reportedly no acid leaked. They put out the fire in 20 minutes.

**2010-11-20 Honeywell, Amherstburg, Ontario.**<sup>116</sup> 45 -100 gal. HF released. A white gas cloud formed over the Honeywell property. The plant's mitigation system kicked in, reportedly knocking it down before it drifted off the property. A faulty three-inch pipe elbow appears to be responsible.

**2010-12 Atmel Plant, Colorado Springs, CO.**<sup>117</sup> Five people were sent to the hospital after getting exposed to HF vapor.

**2010-12-23 Honeywell, Illinois.**<sup>118</sup> HF leak, no details. The probable source was a valve that partially opened improperly. No injuries were reported; Honeywell claims the plant's emission control system captured most of the HF.

**2011-02-11 Transportation Leak, St Clair, Missouri.**<sup>119</sup> Unspecified "large quantity" HF leaked. I-44 was shut down after a "large quantity" of hydrofluoric acid and ammonia began leaking from a semi truck trailer that was legally hauling the chemicals. "The driver of the truck suffered minor chemical inhalation injuries. ... He seemed to be fine..." [SH: this was written right after the incident. HF effects can develop later, even though victims initially "seem fine."]

**2011-02-17 Chalmette Refining (1376), Chalmette, LA.**<sup>120</sup> 2 lb. HF released. A pinhole leak in a release valve released Isobutane and Hydrofluoric Acid.

**2011-03-10 Zhejiang Hailan Chemical Co., Ltd., Hangzhou, China.**<sup>121</sup> 20 (long) tonnes of toxic hydrofluoric acid leaked. Company workers and nearby residents were evacuated. Little info avail.

**2011-03-17 Sunoco Philadelphia Refining Complex, PA.**<sup>122</sup> 1 lb. HF (or MHF) released. 1 worker injured. The accident was attributed to "human error."

**2011-05-11 Precision Castparts, Portland, OR.**<sup>123</sup> Unreported amount of HF released. A power outage caused an air-scrubbing system to fail. After the electricity went out, the company switched to a backup generator but was unable to power up the pollution-control equipment because contamination in the chemical mill prevented access. Two firefighters put on protective suits and oxygen tanks to enter the chemical mill room to try to fix the problem. But the high-voltage box for the scrubber wasn't accessible without an electrician, the company says, and no electrician at the plant was certified to use the protective gear. The firefighters in the mill room pushed a reset button, but nothing happened. Precision Castparts officials say they're not sure why... and they plan to replace its circuitry. Three months later they were still using it without repair, because they say it had performed without glitches since the incident. However, the company had identified an outside service with an electrician certified in HazMat protective gear who could arrive within two hours. *The gas built up in the plant and a highly corrosive mix of nitric acid and hydrofluoric acid was released and formed a cloud.* A request for an emergency reverse 9-1-1 call by Clackamas County Fire went to dispatch centers but somewhere along the line the emergency alert was lost and not even residents who live right across the street from the plant were called. A supervisor at Portland's Bureau of Emergency Communications did not know how to activate a reverse 9-1-1 phone system that could have warned nearby residents last week of chemical fumes escaping from Precision Castparts, according to a city review of what went wrong. The BOEC supervisor on duty contacted the wrong bureau to activate the system. The supervisor contacted the Portland Police Bureau to put in place its Portland Emergency Notification System, but that system became defunct in July 2009, the city analysis showed. The BOEC supervisor was not aware that Portland's new FirstCall system was activated in December 2010, under the oversight of Portland's Office of Emergency Management. "During the incident there was a lack of adequate and clear communication between the multiple agencies as it related to the community notification system", the city's analysis said. Further, BOEC and Portland's Office of Emergency Management lacked clear written protocols for activating the new FirstCall

system. The system is managed by POEM and the Portland Water Bureau. When activated, it can notify residents in a geographic area through published land line phone numbers, unpublished numbers, cell phone numbers and e-mail addresses that residents allow into the system.

**2012-03-05 CITGO Refinery, Corpus Christi, TX.**<sup>124</sup> Between 300 - 500 lb. HF was released. No injuries reported. The leak occurred due to the failure of the seal on a 12 inch flange on a process vessel in the Alkylation unit. The release can be traced to leaks at this flange reported as far back as September 2011. The leak was repaired a few times and parts ordered but not put in place. The leak worsened and eventually, the release was detected by sensors that triggered the alkylation unit's automatic water cannons, designed to capture airborne HF. Automatic water cannons are intended as the last line of defense in the event of a release of HF.



**2012-09 South Korea (Chemical Plant)**<sup>125</sup> (photo, above). 8 tons (2000 gallons or 16,600 lb.) released, 5 killed, 12 hospitalized, maximum stay 10 days.<sup>126</sup> 12,243 treated, thousands evacuated for weeks. A tanker spill released eight tons of hydrofluoric acid, killing five, severely injuring 18.<sup>127</sup> Although near a city, luckily the prevailing wind carried the HF cloud towards the countryside and villages. "A total of 6,982 people were treated at a private medical institution for physical symptoms caused by the hydrogen fluoride spill from September 27 to October 21, 2012, and an additional 5,261 people visited the temporary on-site clinic provided by the Gumi Municipal Government; thus, a total of 12,243 people were treated for fluoride-related symptoms."<sup>128</sup> The accident also contaminated crops and sickened livestock. Around 80 other firms in the area were affected, with business damages estimated at more than \$20 million (£12.5 million). The initial government response to the accident was criticized because of mistakes by firefighters and a sluggish evacuation of nearby residents. The area around the plant was declared a 'special disaster zone.' After that, information about the aftermath of the accident slowed to a trickle. Police said the accident occurred because workers had been directed to save time and did not follow proper safety procedures. Prosecutors plan to indict three Hube Global executives. A video showing the beginning of the accident is available online.<sup>129</sup>

**2012-12-03 Valero Energy Corp. Refinery, Memphis, TN.** Unreported amount HF released, 1 worker dead, 1 injured, 2 firefighters hospitalized.<sup>130</sup> Fire officials reported the workers were exposed to a mixture of propane and hydrofluoric acid when a sight glass in the alkylation unit ruptured.<sup>131</sup>

**2013-01-03 Valero Refinery, Wilmington, CA.**<sup>132</sup> 1-lb. HF in a 78% solution released as a liquid, not gas, (temp 50°F), 2 injuries, 1 requiring medical attention, attributed to human error and poor maintenance.

**2013-04-16 Chalmette Refining (1376), Chalmette, LA.**<sup>133</sup> < 1b. HF released. A hydrofluoric acid leak at a flange on the alkylation unit was discovered during start up.

**2014-07-29 Valero Refinery, Wilmington, CA.**<sup>134</sup> 1-lb. HF released as a gas from a piping system, (temp 72°F), 1 injury, attributed to equipment failure.

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